PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C03C 10/04, A61K 6/06, C03B 32/02, 17/06

A2

(11) International Publication Number: WO 00/34196

(43) International Publication Date: 15 June 2000 (15.06.00)

(21) International Application Number: PCT/US99/29260

(22) International Filing Date: 10 December 1999 (10.12.99)

(30) Priority Data:

60/111,872	11 December 1998 (11.12.98)	US
60/122,558	2 March 1999 (02.03.99)	US
60/153,916	14 September 1999 (14.09.99)	US

(71) Applicant: JENERIC/PENTRON INCORPORATED [US/US]; 53 North Plains Industrial Road, Wallingford, CT 06492–0724 (US).

(72) Inventors: BRODKIN, Dmitri; 75 Herbert Terrace, West Orange, NJ 07052 (US). PANZERA, Carlino; 7 Huntsman Lane, Bellemead, NJ 08502 (US). PANZERA, Paul; 1 Middleton Drive, Mt. Holly, NJ 08060 (US).

(74) Agent: REIMER, Leah, M.; Cantor Colburn LLP, 55 Griffin Road South, Bloomfield, CT 06002 (US).

(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

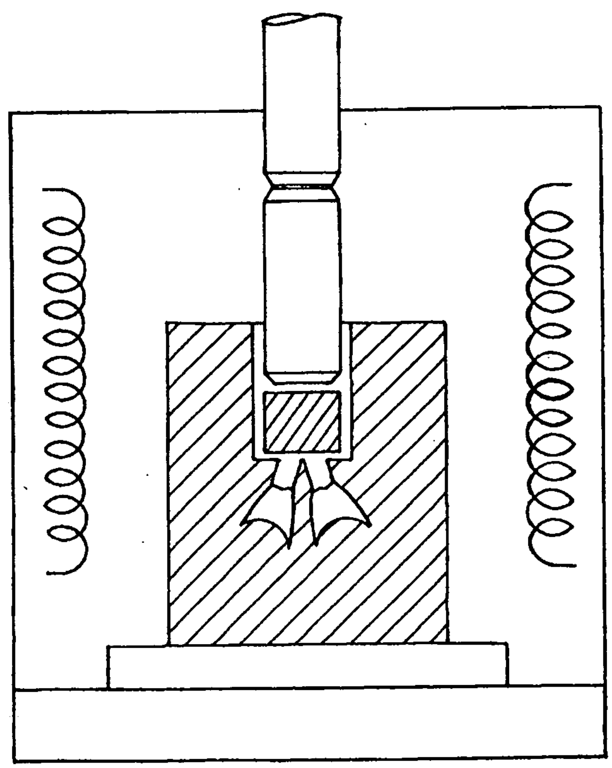
Published

Without international search report and to be republished upon receipt of that report.

(54) Title: PRESSABLE LITHIUM DISILICATE GLASS CERAMICS

(57) Abstract

This invention is directed to lithium disilicate ($Li_2Si_2O_5$) based glass–ceramics comprising silica, lithium oxide, alumina, potassium oxide and phosphorus pentoxide. The glass–ceramics are useful in the fabrication of single and multi–unit dental restorations (e.g. anterior bridges) made by heat pressing into refractory investment molds produced using lost wax techniques. The glass–ceramics have good pressability, i.e., the ability to be formed into dental articles by heat–pressing using commercially available equipment. In accordance with one embodiment directed to the process of making the glass–ceramics, the compositions herein are melted at about 1200° to about 1600 °C, thereafter quenched (e.g., water quenched or roller quenched) or cast into steel molds, or alternately, cooled to the crystallization temperature. The resulting glass is heat–treated to form a glass–ceramic via a one or two step heat–treatment cycle preferably in the temperature range of about 400° to about 1100 °C. The resulting glass ceramics are then pulverized into powder and used to form pressable pellets and/or blanks of desired shapes, sizes and structures which are later pressed into dental restorations.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PRESSABLE LITHIUM DISILICATE GLASS CERAMICS

FIELD OF INVENTION

This invention relates generally to glass-ceramics comprising lithium disilicate and more specifically to glass-ceramics for use in the manufacture of dental restorations and methods of manufacture thereof.

BACKGROUND OF THE INVENTION

The use of lithium disilicate glass ceramics for use in dental restorations has been suggested in the prior art. U.S. Patent No. 4,189,325 to Barret et al. is directed to a glass- ceramic comprising lithium disilicate for use in dental restorations. The glass ceramic requires the presence of Nb_2O_5 and Pt as nucleation agents. Barrett et al. introduced dental restorations made from castable lithium disilicate glass-ceramics in the Li_2O-CaO-Al_2O_3-SiO_2 system nucleated by Pt and Nb_2O_5. According to Barret et al., dental restorations are made by casting a melt into an investment mold, and devitrifying thereafter.

U.S. Patent No. 4,515,634 to Wu et al. is directed to a castable glass-ceramic composition wherein the glass is melted and cast into a shape and is crystallized after it has been shaped. Therefore, the crystallization process is performed by the technician making the restoration, not the manufacturer of the dental material. Wu set al. suggests one way to improve properties of castable lithium disilicate dental

restorations within the same Li_2O-CaO-Al_2O_3-SiO_2 system as described by Barrett et al. is by utilization of P_2O_5 as a nucleating agent. Both Barrett et al. and Wu et al. describe castable compositions having CaO as an essential ingredient believed to improve chemical durability of the resulting glass-ceramics. Chemical durability is one of the major issues that the Wu and Barrett inventions fail to address. For example, total alkali leaching rates for materials presented in Wu's examples were four to five times higher than those for commercial dental porcelain.

Castable dental ceramics as described in Barret et al. and Wu et al. employ melting glass ingots supplied by a manufacturer and casting dental articles into a refractory investment mold. Following the casting process, the cast articles are devitrified (crystallized) by the required heat-treatment steps. This process is very similar to casting metals whereby a heat-treatment step follows the casting process to increase hardness and strength.

U.S. Patent Nos. 5,507,981 and 5,702,514 to Petticrew teach lithium disilicate compositions for use in dental restorations, but the method described therein implies forming glass into the shape of a dental restoration at temperatures much higher than the melting temperature of lithium disilicate and heat-treating the dental restoration after forming to convert the glass into a glass-ceramic.

German Patent Application No. DE19647739 to Schweiger et al. is directed to lithium disilicate compositions for use in dental restorations. The glass-ceramic bodies or blanks used to press dental restorations are defined as "sinterable glass ceramics" which are produced from the starting amorphous glass powder by simultaneous sintering and powder crystallizing, which process is also known as surface crystallization. The glass must be in powder form to be crystallized. Additionally, the lithium disilicate compositions therein require the presence of La_2O_3, MgO and ZnO.

Many of the lithium disilicate compositions in the prior art require casting of the glass into the desired shape and crystallizing thereafter. The glass must be formed into the finally desired shape and thereafter heat treated to crystallize into a lithium disilicate phase. This may result in structural and other problems, since the microstructure is not formed by the dental materials manufacturer, but by the

technician fabricating the dental restoration. Overprocessing by a technician may change the microstructure of the material to something not preferred or desired by the dental materials manufacturer. Moreover, some of the prior art compositions require the forming of the glass ceramics by surface crystallization, limiting the forming and compositional possibilities of the material.

It is desirable to provide a lithium disilicate glass-ceramic which is pressable after the lithium disilicate is formed. It is beneficial to provide a lithium disilicate glass ceramic for use in the fabrication of dental restorations wherein crystallization is carried out by the dental materials manufacturer in the most controlled manner. It is beneficial to provide translucent lithium disilicate glass ceramics having high strength and good presssability.

SUMMARY OF THE INVENTION

This invention is directed to lithium disilicate ($Li_2Si_20_5$) based glass-ceramics comprising silica, lithium oxide, alumina, potassium oxide and phosphorus pentoxide in addition to other components listed below. The glass-ceramics are useful in the fabrication of single and multi-unit dental restorations including but not limited to orthodontic appliances, bridges, space maintainers, tooth replacement appliances, splints, crowns, partial crowns, dentures, posts, teeth, jackets, inlays, onlays, facing, veneers, facets, implants, abutments, cylinders, and connectors made by heat pressing into refractory investment molds produced using lost wax techniques. The glass-ceramics have good pressability, i.e., the ability to be formed into dental articles by heat pressing, also known as hot pressing, or injection molding, using commercially available equipment.

In accordance with one embodiment directed to the process of making the glass-ceramics, the compositions herein are melted at about 1200° to about 1600°C and preferably in the range of about 1300° to about 1400°C for a period of time, preferably for about 4 hours and thereafter quenched (e.g., water quenched or roller quenched) or cast into steel molds, or alternately, cooled to the crystallization temperature.

The resulting glass is heat-treated to form a glass-ceramic via a one or two

step heat-treatment cycle preferably in the temperature range of about 400° to about 1100°C. This crystallization heat treatment may comprise a nucleation step and a crystal growth step. Depending on the composition, the first, nucleation step, may be carried out in the range of about 450°C to about 700°C and preferably in the range of about 500°C to about 650°C for about 0.5 to about 4 hours and the second, crystal growth step, may be carried out in the range of about 800°C to about 1000°C and preferably in the range of about 830°C to about 930°C for about 0.5 to about 48 hours. The most preferable heat treatment comprises about a one hour soak at about 645°C and a subsequent four hour soak at about 850°C.

The resulting glass ceramics are then pulverized into powder and used to form pressable pellets and/or blanks of desired shapes, sizes and structures. Additives may be mixed with the powder prior to forming into pellets or blanks. These pellets and blanks may be used for pressing cores or other frameworks or shapes for dental restorations. The blank or pellet may be subjected to viscous deformation at a temperature in the range of about 800° to about 1200°C, and more preferably in the range of about 850° to about 950°C, and most preferably at less than about 930°C, under vacuum and with the application of pressure of between about 2 to about 8 bar (0.2 to 0.8 MPa) and preferably no greater than about 6 bar (0.6 MPa) to obtain a dental restoration. Moreover, it is possible that the blanks may be machined to a dental restoration of desired geometry.

BRIEF DESCRIPTION OF THE DRAWINGS

Features of the present invention are disclosed in the accompanying drawing, wherein:

Figure 1 is perspective view of a plunger system in a pressing furnace for use in the fabrication of dental restorations in accordance with the invention.

DESCRIPTION OF THE INVENTION

As will be appreciated, the present invention provides glass-ceramic compositions comprising a glassy matrix and lithium disilicate ($Li_2Si_2O_5$). The glass-ceramics are useful for the fabrication of dental restorations. The compositions of the

lithium disilicate glass-ceramics comprise inter alia, silica, lithium oxide, alumina, potassium oxide and phosphorus pentoxide in the ranges given in Table 1 below. The glass-ceramic compositions of the invention have a combination of properties useful for dental restorations. The glass-ceramics have good pressability, i.e., the ability to be formed into dental articles by heat pressing, also known as hot pressing, or injection molding, using commercially available equipment.

Pressable ceramics employ some form of hot-pressing or injection-molding of the glass-ceramic materials, which are typically in the form of pellets. The pellets contain one or more crystalline phases and their morphology as well as volume fraction are not significantly altered in the course of pressing. One reason for this is that the pressing temperature is typically lower than the melting temperature of the crystalline phases. This is a major advantage because microstructure is formed in the controlled conditions by the manufacturer of the glass-ceramic materials, e.g., pellets. Following pressing, the resulting dental article does not require crystallization heat-treatment.

The glass-ceramic pellets can be formed by a number of processes: (1) Glass can be cast into the shape of pellet. Pellets are taken from the mold and crystallized. These pellets can not be shaded by the addition of pigments. (2) Glass can be crystallized in bulk and subsequently milled into powder. Pigments and other additives can be added to the powder. The powder is formed into a pellet and partially or fully sintered. Pigments, if added, create color centers that impart a certain color to a translucent body of the dental article pressed from the pellet. The mechanism of crystallization in the two processes described above is volume crystallization.

Alternatively, surface crystallization may be utilized to crystallize a portion of the glass into one or more crystal phases. This involves milling glass into powder. Pigments and other additives can be added to the powder. This glass powder (amorphous, not crystalline) is formed into a pellet. The glass pellet is sintered and crystallized in the same firing cycle. Not all glass-ceramic materials can be crystallized and sintered simultaneously. Only certain materials and compositions prone to surface crystallization can be processed this way. The glass-ceramics processed from glass powder via simultaneous sintering and crystallization are

sometimes called "sintered" glass-ceramics. Another term that can be used is "sinterable" glass-ceramics.

The compositions herein are prepared by mixing, in the desired proportions, the oxides and/or compounds that decompose to form the oxides, followed by fusing the ingredients to obtain the compositions in Table 1 (ranges in Table 1 are approxiamte). Convenient raw material include lithium carbonate, silica, alumina, carbonates of K, Na, Ca, ammonium phosphate, tricalcium aluminate, aluminum phosphate or aluminum metaphosphate and if necessary, Ta_2O_5, CeO_2, Tb_4O_7, titanium dioxide, and zirconium dioxide.

Table 1

Oxide	Range 1	Range 2	Range 3	Range 4	Range 5	Range 6
SiO_2	62 to 85	64 to 70	62-85	64-70	64 to 70	62 to 76
B_2O_3	0 to 4.9	0 - 2.7	0-4.9	0-2.7	0.5 - 3.0	0 - 5
Al_2O_3	1.5 to 10	1.5 to 6.0	5.1-10	5.2-9.0	1.5 to 6.0	1.5 to 10
F	0 to 1.5	0 to 1.5	0 to 1.5	0 to 1.5	0 to 1.5	0 to 1.5
ZnO	0 to 5	0 to 2	0-5	0-2	-	0 to 5
CaO	0 to 7	0 to 0.9	0-7	0-0.9	0 to 0.9	0 to 7
MgO	0 to 2	0 to 2	0 to 2	0 to 2	-	0 to 2
BaO	0 to 7	0 to 7	0 to 7	0 to 7	0 to 7	0 to 7
SrO	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1
Cs_2O	0 to 5	0 to 5	0 to 5	0 to 5	0 to 5	0 to 5
Li_2O	8 to 19	10 to 15	8-19	10-15	10 to 15	8 to 19
K_2O	2.5 to 7	2.5 to 5	0-7	0-5	2.2 to 5	0 to 7
Na_2O	0 to 5	0 to 3	0-5	0-3	0.5 to 3	0 to 5
TiO_2	0 to 2	0 to 2	0 to 2	0 to 2	0 to 2	0 to 2
ZrO_2	0 to 3	0 to 3	0 to 3	0 to 3	0 to 3	0 to 3
P_2O_5	0.5 to 12	2 to 7	0.5-12	2-7	2 to 7	0.3 to 7.0
SnO_2	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1
Sb_2O_3	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1
Y_2O_3	0 to 3	0 to 3	0 to 3	0 to 3	0 to 3	0 to 3
CeO_2	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1
Eu_2O_3	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1
Tb_4O_7	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1	0 to 1
Nb_2O_5	0 to 2	0 to 2	0 to 2	0 to 2	0 to 2	0 to 2
Ta_2O_5	0 to 2	0 to 2	0 to 2	0 to 2	0 to 2	0.5 to 8.0

The compositions in Table 1 are melted at about 1200° to about 1600°C and preferably in the range of about 1300° to about 1400°C for a period of time, preferably for about 4 hours and thereafter quenched (e.g., water quenched or roller quenched), cast into steel molds, or alternately, cooled to the crystallization

temperature. If the melt is cooled to the crystallization temperature, it may remain in the same furnace.

The resulting glass is heat-treated to form glass-ceramics using a one or a two step heat-treatment cycle preferably in the temperature range of about 400° to about 1100°C. This crystallization heat-treatment may comprise a nucleation step and a crystal growth step. Depending on the composition, the first, nucleation step, may be carried out in the range of about 450°C to about 700°C and preferably in the range of about 500°C to about 650°C for about 0.5 to about 4 hours and the second, crystal growth step, may be carried out in the range of about 800°C to about 1000°C and preferably in the range of about 830°C to about 930°C for about 0.5 to about 48 hours. The most preferable heat treatment comprises about a one hour soak at about 645°C and a subsequent four hour soak at about 850°C.

The glass ceramics comprise lithium disilicate. The resulting glass ceramics are then pulverized into powder sieved to –200 mesh to provide powder with average particle sizes of about 30 to about 40 microns. Pigments, fluorescing agents, opacifying agents, and the like may be added to the powder in a wide range in an amount between about 0 and about 6 wt% and preferably in the amount of between about 0 and about 5 wt% and most preferably in the amount of about 0% to about 3 wt%. Moreover, reinforcing agents may be added to the powder in an amount of from about 0 to about 30 vol % and more preferably in an amount of from about 0 to about 20 vol %. The reinforcing agents may include fibers, whiskers, and particulate fillers and may be fabricated of any known material, preferably a glass or ceramic material.

The powders may be used to form and fuse pressable pellets and/or blanks of desired shapes, sizes and structures. These pellets and blanks may be used for pressing cores or other frameworks or shapes for dental restorations. The blank or pellet may be subjected to viscous deformation at a temperature in the range of about 800° to about 1200°C, and more preferably in the range of about 850° to about 950°C, and most preferably at less than about 930°C, under vacuum and with the application of pressure of between about 2 to about 8 bar (0.2 - 0.8 MPa) and preferably no greater than about 6 bar (0.6 MPa) to obtain a dental restoration. Moreover, it is possible that the blanks may be machined to a dental restoration of desired geometry using

commercially available milling equipment such as the Maho HGF 500 5 Axis CNC Milling Machine available from Fraunhofer Institut Produktionstechnologie, Germany.

In an alternative method herein, the compositions in Table 1 are melted at about 1200° to about 1600°C and preferably in the range of about 1300° to about 1400°C for a period of time, preferably for about 4 hours and thereafter water quenched or cast into steel molds.

The quenched glass is comminuted to a powder. Pigments, fluorescing agents, opacifying agents, and the like may be added to the powder in a wide range in an amount between about 0 and about 6 wt% and preferably in the amount of between about 0 and about 5 wt% and most preferably in the amount of about 0% to about 3 wt%. Moreover, reinforcing agents may be added to the powder in an amount of from about 0 to about 30 vol % and more preferably in an amount of from about 0 to about 20 vol %. The reinforcing agents may include fibers, whiskers, and particulate fillers and may be fabricated of any known material, preferably a ceramic material.

The powder is compacted into a pellet or starting blank. The blank is thereafter simultaneously sintered and crystallized. Heat treatment may be one or more cycles in the temperature range of about 400° to about 1100°C. The crystallization may comprise a nucleation step and a crystal growth step. Depending on the composition, the first, nucleation step, may be carried out in the range of about 450°C to about 700°C and preferably in the range of about 500°C to about 650°C for about 0.5 to about 4 hours and the second, crystal growth step, may be carried out in the range of about 800°C to about 1000°C and preferably in the range of about 830°C to about 930°C for about 0.5 to about 48 hours. The most preferable heat treatment comprises about a one hour soak at about 645°C and a subsequent four hour soak at about 850°C.

The blank or pellet may be subjected to viscous deformation at a temperature in the range of about 800° to about 1200°C, and more preferably in the range of about 850° to about 950°C, and most preferably at less than about 930°C, under vacuum and with the application of pressure of about between about 2 to about 8 bar (0.2 - 0.8 MPa) and preferably no greater than 6 bar (0.6 MPa) to obtain a dental restoration.

Moreover, it is possible that the blanks may be machined to a dental restoration of desired geometry.

To achieve the required combination of properties, namely sufficient strength, formability below 950°C, by heat-pressing using commercially available dental presses such as the Autopress® Plus available from Jeneric/Pentron, Wallingford, CT, translucency and chemical durability, the optimal chemical combinations and crystallization treatment of the present invention are necessary. The best properties are obtained when the lithium metasilicate (Li_2SiO_3) and silica phases are nearly absent, the volume fraction of Li_3PO_4 is less than about 5% and the volume fraction of lithium disilicate ($Li_2Si_2O_5$) is between about 35% and about 60%. High aspect ratio morphology of the lithium disilicate phase is important and is believed to enhance mechanical properties, i.e., strength and fracture toughness of the glass-ceramic.

Li_2O and SiO_2 are instrumental in crystallizing the required amount of the lithium dislicate phase in the compositions of the present invention. Additionally, BaO and Cs_2O stabilize the residual glass and boost the refractive index of the residual glass to match that of lithium disilicate. Al_2O_3 and to a lesser extent, B_2O_3, if less than 3%, yield chemically durable glass-ceramics that exhibit a sufficiently low solubility. Alkali (Na, K, Cs) and alkaline earth metal (Ca, Ba) oxides are required to lower processing temperatures of the glass-ceramic. However some of them affect chemical durability more than others. With respect to the following group of alkali metals and alkaline earth metals of potassium, calcium, sodium, and barium; potassium is associated with the smallest decrease in chemical durability of lithium containing glasses, with calcium being next, and sodium and barium affecting chemical durability the most. However, the best combination of properties is achieved when those oxides are used in combination to achieve the so-called "mixed alkali effect." F lowers the viscosity of the glass-matrix and enhances formability at temperatures below about 950°C. Y_2O_3 in combination with Ce_2O_3, Eu_2O_3 and Tb_4O_7 modify the refractive index as well as impart fluorescence. Nb_2O_5 and Ta_2O_5 modify the refractive index as well as aid nucleation and chemical durability of the resulting glass ceramics.

The following Table 2 illustrates examples of the compositions of the invention.

Table 2

Oxide, wt%	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex.5	Ex. 6	Ex. 7	Ex.8	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13	Ex.14	Ex. 15
SiO_2	68.8	70.0	70.1	65.4	70.7	70.9	68.1	69.5	72	69.0	68.8	65	67.2	68.9	72
B_2O_3	1.2	1.0	------	------	------	------	------	1.3	2.9	------	1.3	1.0	1.2	0.9	2.0
Al_2O_3	4.8	4.9	5.2	8.1	5.3	5.3	4.7	4.8	5.1	6.0	4.8	5	4.7	4.7	4.5
F	------	------	------	1.4	0.2	------	------	------	------	------	------	------	------	------	------
ZnO	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
CaO	0.9	0.5	2.2	------	------	------	2.0	2.0	------	------	1.0	1	1	0.5	0
MgO	------	------	------	------	------	------	------	------	------	------					
BaO	2.8	1.4	------	3.8	5.4	5.4	------	------	2.0	2.7	2.8	2.7	2.7	1.4	2.0
SrO	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Cs_2O	------	------	------	4.1	4.9	4.9	------	------	------	------	------	------	------	------	------
Li_2O	14.4	14.7	14.7	13.4	11.0	10.8	14.3	14.6	13.0	15.3	14.4	15	14.1	14.3	13.0
K_2O	2.5	2.5	4.6	1.7	------	------	4.4	4.5	2.0	2.1	2.2	2.2	2.2	2.0	2.0
Na_2O	1.4	1.4	------	------	------	------	------	------	------	------	1.5	1.4	1.4	1.3	------
TiO_2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
ZrO_2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
P_2O_5	3.3	3.6	3.4	2.7	2.7	2.7	3.3	3.4	3.0	4.0	3.3	3.5	3.2	3.5	3.0
SnO_2	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Sb_2O_3	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Y_2O_3	------	------	------	------	------	------	------	------	0.5	0.8	------	------	------	------	0.5
CeO_2	------	------	------	------	------	------	0.4	------	0.5	------	------	0.4	0.4	0.3	0.6
Eu_2O_3	------	------	------	------	------	------	------	------	0.5	------	------	------	------	------	0.6
Tb_4O_7	------	------	------	------	------	------	0.8	------	------	------	------	0.9	------	0.3	------
Nb_2O_5	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Ta_2O_5	------	------	------	------	------	------	2.0	------	------	------	------	1.9	2.0	1.8	------
Three-Point Flexural Strength*, MPa										430±70	420±60		440±60		400±50
As-pressed Opacity **										50	42		25		34
CTE ***		10.4								8.7	10.1-10.6		10.5	10.0	9.9

*per ISO 6872,

**(relative opacity units)

*** (25°C-500°C), 10^{-6}°C^{-1}

The following examples illustrate the invention.

Examples

Glass-ceramic compositions of the present invention were utilized to make glass-ceramic pellets. These pellets were used to make rectangular bars and rods for measuring the flexural strength by heat-pressing these pellets into the cavity of the refractory investment mold. The process was the same as that used to make dental restorations. The three-point flexure strength was greater or equal to 300 MPa. This strength is sufficient for multi-unit restorations such as anterior bridges. The compositions have a significant amount of glass phase, i.e., approximately 50% glass phase which enhances the pressability thereof.

Moreover, the closeness of refractive indices of the matrix glass (~1.5) and that of the crystallized phase - lithium disilicate - (~1.55) allows for the possibility of translucent glass-ceramics. Specifically in the present invention, the refractive index of the glass matrix is increased to match that of the lithium disilicate phase by adding small amounts of heavy ions such as, but not limited to, Sr, Y, Nb, Cs, Ba, Ta, Ce, Eu and Tb.

The following examples in Table 3 illustrate the effect of different additions on translucency, strength and reactivity with investment of the resulting glass ceramics. The composition of Example 11 (Table 2) was selected as a control composition for the purposes of this study. This composition was modified by adding 0.13 mole% of CeO_2, or 0.06 mole% of Tb_4O_7, or 0.26 mole% of Ta_2O_5, or La_2O_3, or Y_2O_3; and combinations of the latter with CeO_2. Opacity was measured on the pressed disk using an optical densitometer. Reactivity with investment was evaluated qualitatively by visual inspection of disks and copings prior to and after sand-blasting of the reaction layer. Surfaces of the disks were inspected for pittings under low-magnification (8x) stereomicroscope. Compositions comprising combinations of Ta_2O_5, and CeO_2 were found to have the best combination of high translucency (low opacity) and low reactivity with the investment.

Table 3

Oxide, wt%	Ex.11	Ex.16	Ex.17	Ex.18	Ex.19	Ex. 20	Ex.	Ex. 22	Ex.13*	Ex.23
SiO_2	68.8	68.12	68.5	68.2	67.5	67.8	67.9	68.0	67.2	67.5
B_2O_3	1.3	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Al_2O_3	4.8	4.7	4.8	4.7	4.7	4.7	4.7	4.7	4.7	4.7
CaO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
BaO	2.8	2.7	2.8	2.7	2.7	2.7	2.7	2.7	2.7	2.7
Li_2O	14.4	14.3	14.3	14.3	14.1	14.2	14.2	14.2	14.1	14.1
K_2O	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
Na_2O	1.5	1.4	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.4
P_2O_5	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.2	3.3
Y_2O_3	------	1.04	------	-----	------	------	1.04	------	------	-----
CeO_2	------	------	0.39	------	------	------	0.39	0.39	0.39	0.39
Tb_4O_7	------	------	------	0.85	------	------	------	0.85	-----	------
Ta_2O_5	------	------	------	------	2.02	------	------	------	2.01	------
La2O3	------	------	------	------	------	1.5	------	------		1.49
3-pt Flexure Strength per ISO 6872, MPa	420±60								440±60	
As-Pressed Rod 3-pt Flexure Strength, MPa	370±40								370±30	
As-pressed Opacity (relative opacity units)	42	35	39	37	27	25	31	32	25	24
Reactivity with investment material	-----	Medium	Lower	Higher	Medium	Higher	Lower	Medium	Lower	The Highest

*Correspond to compositions in Table 2.

Pellets of the compositions of Examples 2, 11, 13 and 14 were used to press a variety of dental articles in the AutoPress® dental press (Jeneric/Pentron, Wallingford, CT) at pressing cycles carried out under vacuum and involving heating from 700°C to 920°C and holding the temperature for 20 minutes prior to initiation of the pressing cycle. Pressure of 0.5 MPa was applied for 7 minutes through a mold-plunger assembly schematically shown in Figure 1. The plunger assembly used to press the pellets into dental restorations may be the system set forth in copending commonly assigned application Serial No. 09/431,659, filed November 1, 1999, which is hereby incorporated by reference. Disks of compositions of examples 11 and 13 were pressed as described above and chemical solubility was measured according to ISO 6872 and found to be significantly lower than the acceptable limit of 100 ug/cm^2.

The glass-ceramics of the present invention have the capability to be pressed into a single or multi-unit dental restorations at temperatures below about 950°C using already

existing, commercially available equipment such as the Autopress®available from Jeneric/Pentron, Wallingford, CT. Pressability or ability to flow and be pressed into complex shapes of dental restorations at these temperatures is achieved due to the presence of a sufficient amount of the residual glass in the resulting glass-ceramic, in the range of about 15%-60% by volume. The glass-ceramics of the present invention have the capability to be shaded by admixing pigments to the glass-ceramic powder by methods commonly used for dental porcelains.

As will be appreciated, the present invention provides a simple and effective method for producing lithium disilicate glass-ceramic compositions and dental restorations therefrom. While various descriptions of the present invention are described above, it should be understood that the various features can be used singly or in any combination thereof. Therefore, this invention is not to be limited to only the specifically preferred embodiments depicted herein.

Further, it should be understood that variations and modifications within the spirit and scope of the invention may occur to those skilled in the art to which the invention pertains. Accordingly, all expedient modifications readily attainable by one versed in the art from the disclosure set forth herein that are within the scope and spirit of the present invention are to be included as further embodiments of the present invention. The scope of the present invention is accordingly defined as set forth in the appended claims.

1. A glass-ceramic composition comprising in weight percent:
about 62 to about 85% SiO_2;
about 1.5 to about 10% Al_2O_3;
about 8 to about 19% Li_2O;
about 2.5 to about 7% K_2O; and
about 0.5 to about 12 % P_2O_5.

2. The glass-ceramic composition of claim 1 whereby the glass-ceramic is pressable.

3. The glass-ceramic composition of claim 1 further comprising in weight percent:

up to about 4.9% B_2O_3;
up to about 1.5% F;
up to about 5% ZnO;
up to about 7% CaO;
up to about 2% MgO;
up to about 7% BaO;
up to about 1% SrO;
up to about 5% Cs_2O;
up to about 5% Na2O;
up to about 2% TiO_2;
up to about 3% ZrO_2;
up to about 1% SnO_2;
up to about 1% Sb_2O_3;
up to about 3% Y_2O_3;
up to about 1% CeO_2;
up to about 1% Eu_2O_3;
up to about 1% Tb_4O_7;
up to about 2% Nb_2O_5; and
up to about 2% Ta_2O_5.

4. A dental restoration comprising the glass-ceramic of claim 1.

5. A method of making a lithium disilicate dental restoration comprising:

melting a starting glass composition at temperatures within the range of about 1200 to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

6. A method of making a lithium disilicate dental product comprising:

melting a starting glass composition at temperatures within the range of about 1200 to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank; and

sintering the blank.

7. The method of claim 6 wherein the blank is manufactured to a desired shape and structure.

8. The method of claim 6 wherein the blank is sintered to full density.

9. The method of claim 6 wherein crystallization of lithium disilicate is effected in the glass after the quenching step.

10. The method of claim 6 wherein the powder is sieved to the required mesh size prior to the compacting step.

11. The method of claim 6 further including adding additives to the powder prior to the compacting step.

12. The method of claim 11wherein the additives comprise pigments, fluorescing agents, opacifying agents.

13. The method of claim 12 wherein the additives comprise reinforcing agents.

14. The method of claim 13 wherein the reinforcing agents comprise one of fibers, whiskers, particles and mixtures thereof.

15. The method of claim 13 wherein the reinforcing agents are fabricated of ceramic material.

16. The method of claim 6 wherein the sintering of the starting blank comprises heating to a temperature in the range of about 800° to about 1000°C.

17. The method of claim 6 wherein the sintering of the starting blank comprises heating to a temperature in the range of about 850° to about 950°C.

18. The method of claim 6 wherein the sintered starting blank is subjected to viscous deformation at a temperature in the range of from about 850° to about 950°C under vacuum and at a pressure not exceeding about 6 bar to obtained the desired shape.

19. The method of claim 6 wherein the sintered blank is machined to a dental restoration of desired shape.

20. The method of claim 6 wherein the dental product is a dental core and is provided with one or more coatings.

21. The method of claim 20 wherein the one or more coatings is selected from a ceramic, a sintered ceramic, a glass ceramic, a porcelain, a glass, a glaze, a composite and mixtures thereof.

22. The method of claim 20 wherein the one or more coatings has a firing temperature in the range of about 700° to about 900°C and a coefficent of thermal expansion (measured from room temperature to its transition temperature) of within about $\pm$ 2.0 x 10^{-6}/ °C of the dental product (measured at the same temperature range).

23. The dental restoration of claim 4 formed into a component selected from orthodontic appliances, bridges, space maintainers, tooth replacement appliances, splints, crowns, partial crowns, dentures, posts, teeth, jackets, inlays, onlays, facing, veneers, facets, implants, abutments, cylinders, and connector.

24. A blank for the manufacture of a dental restoration comprising the glass ceramic of claim 1.

25. The method of claim 6 wherein the glass-ceramic comprises in weight percent:

about 62 to about 85% SiO_2;

about 1.5 to about 10% Al_2O_3;

about 8 to about 19% Li_2O;

about 2.5 to about 7% K_2O; and

about 0.5 to about 12 % P_2O_5.

26. The method of claim 25 wherein the glass-ceramic further comprises in weight percent:

up to about 4.9% B_2O_3;

up to about 1.5% F;

up to about 5% ZnO;

up to about 7% CaO;

up to about 2% MgO;

up to about 7% BaO;

up to about 1% SrO;

up to about 5% Cs_2O;

up to about 5% Na_2O;

up to about 2% TiO_2;

up to about 3% ZrO_2;

up to about 1% SnO_2;

up to about 1% Sb_2O_3;

up to about 1% Sb_2O_3;

up to about 3% Y_2O_3;

up to about 1% CeO_2;

up to about 1% Eu_2O_3;

up to about 1% Tb_2O_7;

up to about 2% Nb_2O_5; and

up to about 2% Ta_2O_5.

27. A method of making a lithium disilicate dental product comprising:

melting a starting glass comprising a composition at temperatures within the range of about 1200 to about 1600°C;

cooling the glass melt to the crystallization temperature to form a glass-ceramic;

quenching the glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank; and

sintering the blank.

28. The method of claim 27 wherein the sintering imparts sufficient strength for further handling of the blank.

29. The method of claim 27 wherein the powder is sieved to the required mesh size prior to the compacting step.

30. The method of claim 27 further including adding additives to the powder prior to the compacting step.

31. The method of claim 30 wherein the additives comprise pigments, fluorescing agents, opacifying agents.

32. The method of claim 30 wherein the additives comprise reinforcing agents.

33. The method of claim 32 wherein the reinforcing agents comprise one of fibers, whiskers, particles and mixtures thereof.

34. The method of claim 32 wherein the reinforcing agents are fabricated of ceramic material.

35. The method of claim 27 wherein the sintering of the starting blank comprises heating to a temperature in the range of about 800 to about 1000°C.

36. The method of claim 27 wherein the sintering of the starting blank comprises heating to a temperature in the range of about 850 to about 950°C.

37. The method of claim 27 wherein the sintered starting blank is subjected to viscous deformation at a temperature in the range of from about 850 to about 950°C under vacuum and at a pressure not exceeding about 7 bar to obtained the desired shape.

38. The method of claim 27 wherein the sintered blank is machined to a dental restoration of desired shape.

39. The method of claim 27 wherein the dental product is a core and is provided with one or more coatings.

40. The method of claim 39 wherein the one or more coatings is selected from a ceramic, a sintered ceramic, a glass ceramic, a porcelain, a glass, a glaze, a composite and mixtures thereof.

41. The method of claim 39 wherein the one or more coatings has a firing temperature in the range of about 700 to about 900°C and a coefficent of thermal expansion (measured from room temperature to its transition temperature) of within about $\pm 2.0 \times 10^{-6}$/ °C of the dental product (measured at the same temperature range).

42. The method of claim 39 wherein the glass-ceramic comprises in weight percent:

about 62 to about 85% SiO_2;

about 1.5 to about 10% Al_2O_3;

about 8 to about 19% Li_2O;

about 2.5 to about 7% K_2O; and

about 0.5 to about 12 % P_2O_5.

43. A glass-ceramic composition comprising in weight percent:

about 64 to about 70% SiO_2;

about 1.5 to about 6 Al_2O_3;

about 10 to about 15% Li_2O;

about 2.5 to about 5% K_2O; and

about 2 to about 7 % P_2O_5.

44. The glass-ceramic composition of claim 43 whereby the glass-ceramic is pressable.

45. The glass-ceramic composition of claim 43 further comprising in weight percent:

up to about 1.5% F;
up to about 7% BaO;
up to about 1% SrO;
up to about 5% Cs_2O;
up to about 2.7% B_2O_3;
up to about 2% ZnO;
up to about 0.9% CaO;
up to about 2% MgO;
up to about 3% Na_2O;
up to about 2% TiO_2;
up to about 3% ZrO_2;
up to about 1% SnO_2;
up to about 1% Sb_2O_3;
up to about 3% Y_2O_3;
up to about 1% CeO_2;
up to about 1% Eu_2O_3;
up to about 1% Tb_4O_7;
up to about 2% Nb_2O_5; and
up to about 2% Ta_2O_5.

46. A dental restoration comprising the glass-ceramic of claim 43.

47. A method of making a lithium disilicate dental restoration comprising:

melting a starting glass composition comprising in weight percent

about 64 to about 70% SiO_2;

about 1.5 to about 6 Al_2O_3;

about 10 to about 15% Li_2O;

about 2.5 to about 5% K_2O; and

about 2 to about 7 % P_2O_5; at temperatures within the range of about 1200° to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

48. A glass-ceramic composition comprising in weight percent:

about 62 to about 85% SiO_2;

about 5.1 to about 10 Al_2O_3;

about 8 to about 19% Li_2O; and

about 0.5 to about 12 % P_2O_5.

49. The glass-ceramic composition of claim 48 whereby the glass-ceramic is pressable.

50. The glass-ceramic composition of claim 48 further comprising in weight percent:

up to about 7% K_2O;

up to about 1.5% F;

up to about 7% BaO;

up to about 1% SrO;

up to about 5% Cs_2O;

up to about 4.9% B_2O_3;

up to about 5% ZnO;

up to about 7% CaO;

up to about 2% MgO;

up to about 5% Na_2O;

up to about 2% TiO_2;

up to about 3% ZrO_2;

up to about 1% SnO_2;

up to about 1% Sb_2O_3;

up to about 3% Y_2O_3;

up to about 1% CeO_2;

up to about 1% Eu_2O_3;

up to about 1% Tb_4O_7;

up to about 2% Nb_2O_5; and

up to about 2% Ta_2O_5.

51. A dental restoration comprising the glass-ceramic of claim 48.

52. A method of making a lithium disilicate dental restoration comprising:

melting a starting glass composition comprising in weight percent

about 62 to about 85% SiO_2;

about 5.1 to about 10 Al_2O_3;

about 8 to about 19% Li_2O; and

about 0.5 to about 12 % P_2O_5; at temperatures within the range of about 1200° to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

53. A glass-ceramic composition comprising in weight percent:

about 64 to about 70% SiO_2;

about 5.2 to about 9 Al_2O_3;

about10 to about 15% Li_2O; and

about 2 to about 7 % P_2O_5.

54. The glass-ceramic composition of claim 53 whereby the glass-ceramic is pressable.

55. The glass-ceramic composition of claim 53 further comprising in weight percent:

up to about 1.5% F;
up to about 7% BaO;
up to about 1% SrO;
up to about 5% Cs_2O;
up to about 5% K_2O;
up to about 2.7% B_2O_3;
up to about 2% ZnO;
up to about 0.9% CaO;
up to about 2% MgO;
up to about 3% Na_2O;
up to about 2% TiO_2;
up to about 3% ZrO_2;
up to about 1% SnO_2;
up to about 1% Sb_2O_3;
up to about 3% Y_2O_3;
up to about 1% CeO_2;
up to about 1% Eu_2O_3;
up to about 1% Tb_4O_7;
up to about 2% Nb_2O_5; and
up to about 2% Ta_2O_5.

56. A dental restoration comprising the glass-ceramic of claim 53.

57. A method of making a lithium disilicate dental restoration comprising:

melting a starting glass composition comprising in weight percent

about 64 to about 70% SiO_2;

about 5.2 to about 9 Al_2O_3;

about10 to about 15% Li_2O; and

about 2 to about 7 % P_2O_5; at temperatures within the range of about 1200° to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

58. A glass-ceramic composition comprising in weight percent:

about 64 to about 70% SiO_2;

about 1.5 to about 6 Al_2O_3;

about 10 to about 15% Li_2O;

about 2 to about 7 % P_2O_5;

about 2.2 to about 5% K_2O;

about 0.5 to about 3% Na_2O; and

about 0.5 to about 3% B_2O_3.

59. The glass-ceramic composition of claim 58 whereby the glass-ceramic is pressable.

60. The glass-ceramic composition of claim 58 further comprising in weight percent:

up to about 1.5% F;
up to about 7% BaO;
up to about 1% SrO;
up to about 5% Cs_2O;
up to about 0.9% CaO;
up to about 2% TiO_2;
up to about 3% ZrO_2;
up to about 1% SnO_2;
up to about 1% Sb_2O_3;
up to about 3% Y_2O_3;
up to about 1% CeO_2;
up to about 1% Eu_2O_3;
up to about 1% Tb_4O_7;
up to about 2% Nb_2O_5; and
up to about 2% Ta_2O_5.

61. A dental restoration comprising the glass-ceramic of claim 58.

62. A method of making a lithium disilicate dental restoration comprising:

melting a starting glass composition comprising in weight percent

about 64 to about 70% SiO_2;

about 1.5 to about 6 Al_2O_3;

about 10 to about 15% Li_2O;

about 2 to about 7 % P_2O_5;

about 2.2 to about 5% K_2O;

about 0.5 to about 3% Na_2O; and

about 0.5 to about 3% B_2O_3; at temperatures within the range of about 1200° to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

63. A glass-ceramic composition comprising in weight percent:

about 62 to about 76% SiO_2;

about 1.5 to about 10 Al_2O_3;

about 8 to about 19% Li_2O;

about .3 to about 7% P_2O_5; and

about .5 to about 8% Ta_2O_5.

64. The glass-ceramic composition of claim 63 whereby the glass-ceramic is pressable.

65. The glass-ceramic composition of claim 63 further comprising in weight percent:

up to about 5% B_2O_3.

up to about 5% Na_2O;

up to about 7% K_2O;

up to about 1.5% F;

up to about 5% ZnO;

up to about 2% MgO;

up to about 7% BaO;

up to about 1% SrO;

up to about 5% Cs_2O;

up to about 7% CaO;

up to about 2% TiO_2;

up to about 3% ZrO_2;

up to about 1% SnO_2;

up to about 1% Sb_2O_3;

up to about 3% Y_2O_3;

up to about 1% CeO_2;

up to about 1% Eu_2O_3;

up to about 1% Tb_4O_7; and

up to about 2% Nb_2O_5.

66. A dental restoration comprising the glass-ceramic of claim 63.

67. A method of making a dental restoration comprising:
melting a starting glass composition comprising in weight percent
about 62 to about 76% SiO_2;
about 1.5 to about 10 Al_2O_3;
about 8 to about 19% Li_2O;
about .3 to about 7% P_2O_5; and
about .5 to about 8% Ta_2O_5; at temperatures within the range of about 1200° to about 1600°C;
quenching the glass melt;
subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;
comminuting the glass ceramic to a powder;
compacting the powder to a starting blank;
sintering the blank; and
pressing the blank into the dental restoration.

68. A glass-ceramic composition comprising in weight percent:
about 68.8% SiO_2;
about 1.3% B_2O_3;
about 4.8% Al_2O_3;
about 1.0% CaO;
about 2.8% BaO;
about 14.4% Li_2O;
about 2.2 % K_2O;
about 1.5% Na_2O; and
about 3.3% P_2O_5.

69. The glass-ceramic of claim 68 having a flexural strength of equal to or greater than about 420 MPa.

70. The glass-ceramic composition of claim 68 whereby the glass-ceramic is pressable.

71. A dental restoration comprising the glass-ceramic of claim 68.

72. A method of making a dental restoration comprising:

melting a starting glass composition comprising in weight percent

about 68.8% SiO_2;

about 1.3% B_2O_3;

about 4.8% Al_2O_3;

about 1.0% CaO;

about 2.8% BaO;

about 14.4% Li_2O;

about 2.2 % K_2O;

about 1.5% Na_2O; and

about 3.3% P_2O_5; at temperatures within the range of about 1200° to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400° to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

73. A glass-ceramic composition comprising in weight percent:
about 67.2% SiO_2;
about 1.2% B_2O_3;
about 4.7% Al_2O_3;
about 1.0% CaO;
about 2.7% BaO;
about 14.1% Li_2O;
about 2.2 % K_2O;
about 1.4% Na_2O;
about 3.2% P_2O_5;
about 0.4% CeO_2; and
about 2% Ta_2O_5.

74. The glass-ceramic of claim 73 having a flexural strength of equal to or greater than about 440 MPa.

75. The glass-ceramic composition of claim 73 whereby the glass-ceramic is pressable.

76. A dental restoration comprising the glass-ceramic of claim 73.

77. A method of making a dental restoration comprising:

melting a starting glass composition comprising in weight percent

about 68.8% SiO_2;

about 1.3% B_2O_3;

about 4.8% Al_2O_3;

about 1.0% CaO;

about 2.8% BaO;

about 14.4% Li_2O;

about 2.2 % K_2O;

about 1.5% Na_2O; and

about 3.3% P_2O_5; at temperatures within the range of about 1200° to about 1600°C;

quenching the glass melt;

subjecting the quenched glass to one or more heat treatments in the temperature range of from about 400 to about 1100°C to convert the glass into a glass-ceramic;

comminuting the glass ceramic to a powder;

compacting the powder to a starting blank;

sintering the blank; and

pressing the blank into the dental restoration.

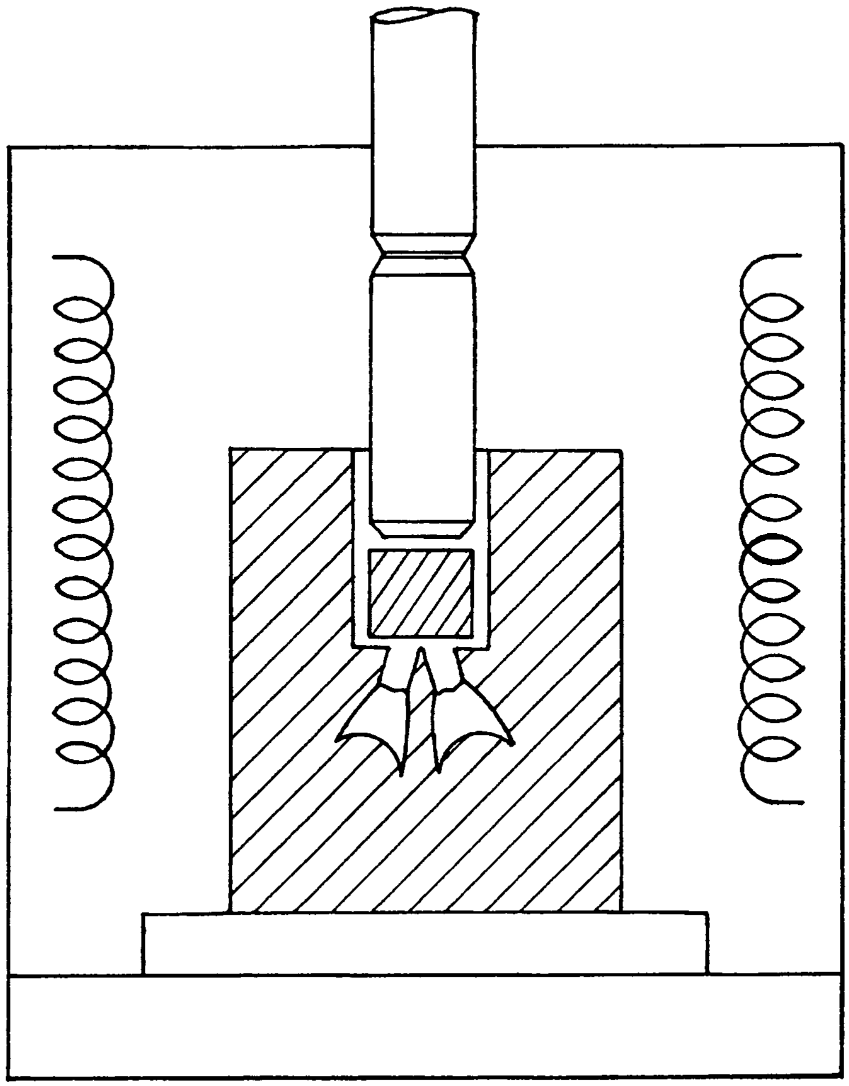


FIG. 1

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [7] : C03C 10/04, A61K 6/06, C03B 32/02, 17/06

A3

(11) International Publication Number: WO 00/34196

(43) International Publication Date: 15 June 2000 (15.06.00)

(21) International Application Number: PCT/US99/29260

(22) International Filing Date: 10 December 1999 (10.12.99)

(30) Priority Data:

60/111,872	11 December 1998 (11.12.98)	US
60/122,558	2 March 1999 (02.03.99)	US
60/153,916	14 September 1999 (14.09.99)	US

(71) Applicant: JENERIC/PENTRON INCORPORATED [US/US]; 53 North Plains Industrial Road, Wallingford, CT 06492-0724 (US).

(72) Inventors: BRODKIN, Dmitri; 75 Herbert Terrace, West Orange, NJ 07052 (US). PANZERA, Carlino; 7 Huntsman Lane, Bellemead, NJ 08502 (US). PANZERA, Paul; 1 Middleton Drive, Mt. Holly, NJ 08060 (US).

(74) Agent: REIMER, Leah, M.; Cantor Colburn LLP, 55 Griffin Road South, Bloomfield, CT 06002 (US).

(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

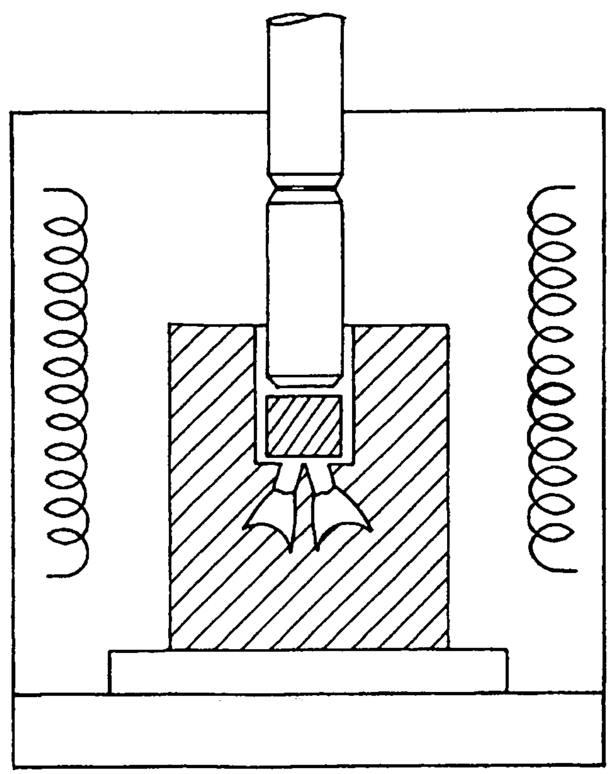
With international search report.

(88) Date of publication of the international search report: 16 November 2000 (16.11.00)

(54) Title: PRESSABLE LITHIUM DISILICATE GLASS CERAMICS

(57) Abstract

This invention is directed to lithium disilicate ($Li_2Si_2O_5$) based glass-ceramics comprising silica, lithium oxide, alumina, phosphorus pentoxide, and optionally potassium oxide or tantalum oxide. The glass-ceramics are useful in the fabrication of single and multi-unit dental restorations (e.g. anterior bridges) made by heat pressing into refractory investment molds produced using lost wax techniques. The glass-ceramics have good pressability, i.e., the ability to be formed into dental articles by heat-pressing using commercially available equipment. In accordance with an embodiment directed to the process of making the glass-ceramics, the starting compositions are melted at about 1200° to about 1600 °C, thereafter quenched (e.g., water quenched or roller quenched) or cast into steel molds, or alternately, cooled to the crystallization temperature. The resulting glass is heat-treated to form a glass-ceramic via a one or two step heat-treatment cycle preferably in the temperature range of about 400° to about 1100 °C. The resulting glass ceramics are then pulverized into powder and used to form pressable pellets and/or blanks of desired shapes, sizes and structures which are later pressed into dental restorations.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/29260

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C10/04 A61K6/06 C03B32/02 C03B17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 827 941 A (IVOCLAR AG) 11 March 1998 (1998-03-11) claims; examples ---	1-4, 23-26, 42-47, 58-62
P,X	EP 0 916 625 A (IVOCLAR AG) 19 May 1999 (1999-05-19) claims; example 14 ---	1-4, 23-26, 42-47
X	EP 0 536 572 A (CORNING INC) 14 April 1993 (1993-04-14) claims; examples ---	1-3, 43-45, 48-50, 53-55, 58-60

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 April 2000	04.08.00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	VAN BOMMEL, L

1

INTERNATIONAL SEARCH REPORT

Intern. ...al Application No
PCT/US 99/29260

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 536 479 A (CORNING INC) 14 April 1993 (1993-04-14) claims; examples ---	1-3, 43-45, 48-50, 53-55, 58-60
X	GB 1 312 700 A (ENGLISH ELECTRIC CO LTD) 4 April 1973 (1973-04-04) claims; examples ---	1-3, 43-45, 48-50, 53-55
X	JP 10 188260 A (NGK INSULATORS LTD) 21 July 1998 (1998-07-21) abstract	1-3, 43-45, 48-50
P,X	& US 5 872 069 A (ABE) 16 February 1999 (1999-02-16) claims; examples ---	
X	US 3 816 704 A (BOROM M ET AL) 11 June 1974 (1974-06-11) claims; examples ---	1-3, 48-50
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 268 (C-444), 29 August 1987 (1987-08-29) -& JP 62 072547 A (TOSHIMICHI MORISANE;OTHERS: 01), 3 April 1987 (1987-04-03) abstract; examples ---	1-3, 48-50
X	US 5 820 989 A (WENGERT DECEASED PAUL R ET AL) 13 October 1998 (1998-10-13) claims; examples ---	1-3, 48-50
X	US 5 580 363 A (GOTO NAOYUKI ET AL) 3 December 1996 (1996-12-03) claims; examples ---	1-3
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 081 (C-0915), 27 February 1992 (1992-02-27) -& JP 03 271130 A (ISHIZUKA GLASS CO LTD), 3 December 1991 (1991-12-03) abstract; examples ---	1-3
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 402 (C-633), 6 September 1989 (1989-09-06) -& JP 01 145348 A (TOSHIBA GLASS CO LTD), 7 June 1989 (1989-06-07) abstract; examples --- -/--	1-3

1

Intern nal Application No
PCT/US 99/29260

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 781 731 A (YAMAMURA GLASS CO LTD) 2 July 1997 (1997-07-02) claims; examples -----	48-50

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/29260

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

./.

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-4,23-26,42-77

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-4,23-26,42-77

1.1. Claims: 1-4,23-26,42-47,58-62,68-77
Glass-ceramics comprising specified amounts of SiO_2, Li_2O, Al_2O_3, K_2O and P_2O_5, and methods for their production.

1.2. Claims: 48-57
Glass-ceramics comprising specified amounts of SiO_2, Li_2O, Al_2O_3 and P_2O_5, and methods for their production.

1.3. Claims: 63-67
Glass-ceramics comprising specified amounts of SiO_2, Li_2O, Al_2O_3, P_2O_5 and Ta_2O_5, and methods for their production.

2. Claims: 5-22,27-41

Methods for the production of lithium disilicate glass ceramic products

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/29260

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0827941	A	11-03-1998	DE	19647739	A	12-03-1998
			AT	186286	T	15-11-1999
			AU	695549	B	13-08-1998
			AU	3530597	A	26-03-1998
			CA	2213390	A	05-03-1998
			DE	59700651	D	09-12-1999
			JP	10101409	A	21-04-1998
			US	5968856	A	19-10-1999
EP 0916625	A	19-05-1999	DE	19750794	A	17-06-1999
			JP	11314938	A	16-11-1999
EP 0536572	A	14-04-1993	US	5176961	A	05-01-1993
			DE	69207324	D	15-02-1996
			DE	69207324	T	22-08-1996
			HK	104196	A	21-06-1996
			JP	5208846	A	20-08-1993
			MX	9205735	A	01-05-1993
EP 0536479	A	14-04-1993	US	5219799	A	15-06-1993
			BR	9203278	A	27-04-1993
			DE	69204791	D	19-10-1995
			DE	69204791	T	22-02-1996
			JP	7187710	A	25-07-1995
			MX	9205736	A	01-05-1993
GB 1312700	A	04-04-1973	NONE			
JP 10188260	A	21-07-1998	US	5872069	A	16-02-1999
US 3816704	A	11-06-1974	AU	5233773	A	22-08-1974
			DE	2313347	A	04-10-1973
			FR	2176901	A	02-11-1973
JP 62072547	A	03-04-1987	NONE			
US 5820989	A	13-10-1998	NONE			
US 5580363	A	03-12-1996	JP	2959363	B	06-10-1999
			JP	7157331	A	20-06-1995
JP 03271130	A	03-12-1991	JP	1841819	C	12-05-1994
			JP	5053736	B	10-08-1993
JP 01145348	A	07-06-1989	JP	1831999	C	29-03-1994
			JP	5044417	B	06-07-1993
EP 0781731	A	02-07-1997	DE	69601697	D	15-04-1999
			DE	69601697	T	22-07-1999
			JP	10226532	A	25-08-1998
			US	5691256	A	25-11-1997
			US	5874376	A	23-02-1999